

Method for producing glycerol carbonate methacrylate

The invention relates to a process for preparing glycerol carbonate methacrylate in the presence of 5 metal chelate catalysts of the metal ion 1,3-diketonate type, especially zirconium acetylacetone.

In the coatings industry (2-oxo-1,3-dioxolan-4-yl)-methyl methacrylate (glycerol carbonate methacrylate) 10 is a much-used crosslinker. There are a variety of preparation processes known for glycerol carbonate methacrylate.

JP 2001018729 reacts glycerol carbonate with acryloyl 15 chloride. The chloride wastes produced constitute a large environmental burden. WO 2000031195 reacts glycidyl methacrylate with CO₂. This process is carried out under high pressure. The apparatus needed for the process is intricate and expensive. DE 3937116 reacts a 20 cyclocarbonate-containing alcohol with a carboxylic acid at elevated temperature and in the presence of an acidic catalyst. The desired product is obtained, after distillation, in a purity of 75.5%. The yield varies, as a function of the acid used, between 25.5% and 83%. 25 With the purity achieved therein, of just 75.5%, there are numerous applications in which the product cannot be used.

It was an object of the invention to prepare glycerol 30 carbonate methacrylate in high purity and with high yields.

This object has been achieved by a process for preparing (2-oxo-1,3-dioxolan-4-yl)methyl methacrylate 35 in which methyl methacrylate is transesterified with glycerol carbonate in the presence of stabilizers and a metal chelate catalyst of the metal ion 1,3-diketonate type, especially zirconium acetylacetone.

Surprisingly it has been found that through the use of zirconium acetylacetone as a catalyst it is possible to operate under very mild conditions. The trans-
5 esterification in the presence of zirconium acetylacetone takes place at 50-80°C, preferably at 70°C.

Zirconium acetylacetone is used preferably in amounts of 0.1-5.0% by weight, more preferably of from 1.0-3.0%
10 by weight, based on the total weight of the batch.

As the catalyst it is possible, besides zirconium acetylacetone, to use other metal 1,3-diketonates as well, such as lithium or zinc 1,3-diketonates, for
15 example, or 1,3-diphenylpropane-1,3-dione.

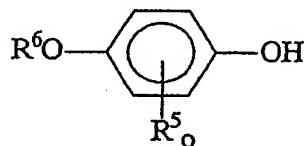
It has been found that through the reaction regime of the invention a low crosslinker content is obtained. The effect of a low crosslinker content in applications
20 is that improved mechanical properties are obtained in the case of copolymerization with other monofunctional monomers. The material is less brittle. Crosslinkers observed include glycerol dimethacrylate and glycerol trimethacrylate. The amount of crosslinker observed in
25 the product is preferably less than 5% by weight, more preferably less than 3% by weight.

Additionally it has been found that the product can be prepared with high yields and in high purity. Yields
30 above 80% are obtained, with product purities of around 90%. The purities achieved mean that costly and inconvenient distillative purification is unnecessary. The monomer possesses a high boiling point and can therefore be separated off only in a high vacuum.
35 Costly and intricate distillation apparatus, and the risk of polymerization under the high thermal load, which is frequently observed with this monomer, both disappear.

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In the preparation of (2-oxo-1,3-dioxolan-4-yl)methyl methacrylate, stabilizers are added, which prevent free-radical polymerization of the (meth)acrylic groups 5 during the reaction. These stabilizers are widely known in the art.

Use is made principally of 1,4-dihydroxybenzenes. Differently substituted dihydroxybenzenes, though, can 10 also be employed. In general such stabilizers can be represented by the general formula (I)



(I),

15 in which

R⁵ is a linear or branched alkyl radical having one to eight carbon atoms, halogen or aryl, preferably an alkyl radical having one to four carbon atoms, more 20 preferably methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, Cl, F or Br;

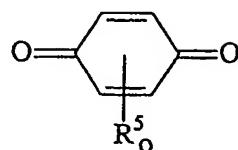
o is an integer in the range from one to four, preferably one or two; and

25

R⁶ is hydrogen, a linear or branched alkyl radical having one to eight carbon atoms or aryl, preferably an alkyl radical having one to four carbon atoms, more preferably methyl, ethyl, n-propyl, isopropyl, n-butyl, 30 isobutyl, sec-butyl or tert-butyl.

An alternative is to use compounds having 1,4-benzo-quinone as their parent compound. Such compounds can be described by the formula (II)

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(II)

in which

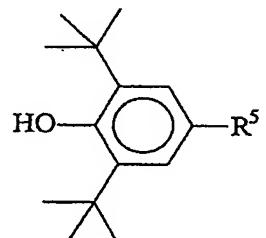
5 R⁵ is a linear or branched alkyl radical having one to eight carbon atoms, halogen or aryl, preferably an alkyl radical having one to four carbon atoms, more preferably methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, Cl, F or Br; and

10

o is an integer in the range from one to four, preferably one or two.

Also used are phenols of the general structure (III)

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(III)

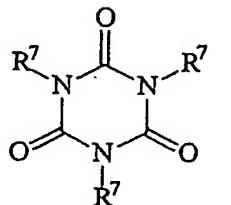
in which

20 R⁵ is a linear or branched alkyl radical having one to eight carbon atoms, aryl or aralkyl, propionic esters with mono- to tetrahydric alcohols, which may also contain heteroatoms such as S, O and N, preferably an alkyl radical having one to four carbon atoms, more preferably methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl or tert-butyl.

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A further advantageous class of substance is represented by hindered phenols based on triazine derivatives of the formula (IV)

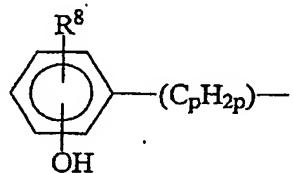
30



(IV)

where R⁷ = compound of the formula (V)

5



(V)

in which

10 R⁸ = C_pH_{2p+1}

where p = 1 or 2.

Employed with particular success are the compounds
 15 1,4-dihydroxybenzene, 4-methoxyphenol, 2,5-dichloro-
 3,6-dihydroxy-1,4-benzoquinone, 1,3,5-trimethyl-2,4,6-
 tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, 2,6-di-
 tert-butyl-4-methylphenol, 2,4-dimethyl-6-tert-butyl-
 phenol, 2,2-bis[3,5-bis(1,1-dimethylethyl)-4-hydroxy-
 20 phenyl-1-oxopropoxymethyl]1,3-propanediyl ester,
 2,2'-thiodiethyl bis[3-(3,5-di-tert-butyl-4-hydroxy-
 phenyl)propionate, octadecyl-3-(3,5-di-tert-butyl-4-
 hydroxyphenyl)propionate, 3,5-bis(1,1-dimethylethyl-
 2,2-methylenebis(4-methyl-6-tert-butyl)phenol, tris
 25 (4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)-s-triazine-
 2,4,6-(1H,3H,5H)trione, tris(3,5-di-tert-butyl-4-
 hydroxy)-s-triazine-2,46-(1H,3H,5H)trione or tert-
 butyl-3,5-dihydroxybenzene, more preferably 4-hydroxy-
 2,2,6,6-tetramethylpiperidinoxy, hydroquinone,
 30 4-methyl-2,6-di-tert-butylphenol, hydroquinone mono-

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methyl ether, 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate, 4-(methacryloyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl or 2,5-di-tert-butylhydroquinone.

5

For the purposes of the invention a tocopherol compound is used to stabilize ethylenically unsaturated monomers.

10 The tocopherol compounds which can be used in the context of the invention are chroman-6-ols (3,4-dihydro-2H-1-benzopyran-6-ols) which are substituted in position 2 by a 4,8,12-trimethyltridecyl radical. The tocopherols which can be used with preference in

15 accordance with the invention include alpha-tocopherol, beta-tocopherol, gamma-tocopherol, delta-tocopherol, zeta₂-tocopherol, and eta-tocopherol, all of the aforementioned compounds each in the (2R,4'R,8'R) form, and also alpha-tocopherol in the (all-rac) form.

20 Preference is given to alpha-tocopherol in the (2R,4'R,8'R) form (trivial name: RRR-alpha-tocopherol), and also to the synthetic racemic alpha-tocopherol (all-rac-alpha-tocopherol). Of these, in turn, the latter is of particular interest owing to the relatively low

25 price.

Based on the weight of the reaction mixture as a whole, the fraction of the stabilizers, individually or as a mixture, is generally 0.01%-0.50% by weight, the 30 stabilizer concentration being selected preferably so as not to be detrimental to the color number in accordance with DIN 55945. Many of these stabilizers are available commercially.

35 Glycerol carbonate methacrylate can be used as a functional monomer in copolymers of coating materials and adhesives, and allows a subsequent, polymer-analogous reaction, including crosslinking with

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difunctional amines in a coating formulation. Furthermore, it can be used in battery electrolytes, in extrusion resins, and for metal extraction.

5 The examples given below are given in order better to illustrate the present invention, but have no capacity to restrict the invention to the features disclosed herein.

10 **Examples**

Example 1

15 118 g (1.0 mol) of glycerol carbonate are heated with 600 g (6.0 mol) of methyl methacrylate and 0.14 g of 4-hydroxy-2,2,6,6-tetramethylpiperidinoxy1 (Tempol) in a round-bottomed flask with distillation apparatus. Any water present is distilled off azeotropically with methyl methacrylate. The mixture is then cooled 20 slightly. 18.0 g of zirconium acetylacetone and the amount of methyl methacrylate equivalent to the azeotrope distillate are added to the mixture. The mixture is heated to boiling. Alcoholysis is commenced at an overhead temperature of 70°C. Toward the end of 25 the reaction it increased to 100°C.

30 After the end of the alcoholysis the mixture is cooled and the zirconium acetylacetone catalyst is precipitated with dilute phosphoric acid. The suspension is then passed through a pressure filter and the filtrate is separated off.

35 For the purpose of separating off the glycerol carbonate, the filtrate is shaken in a separating funnel containing a dilute NaCl solution. The filtrate is degassed on a rotary evaporator at 70°C and 200-10 mbar.

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The yield is 80.6%. The purity of the product is 91.4%.

Experiment number: B1

5 **Example 2**

236 g (2.0 mol) of glycerol carbonate are heated with 1200 g (12.0 mol) of methyl methacrylate and 0.29 g of 4-hydroxy-2,2,6,6-tetramethylpiperidinoxy (Tempol) in 10 a round-bottomed flask with distillation apparatus. Any water present is distilled off azeotropically with methyl methacrylate. The mixture is then cooled slightly. 28.7 g of zirconium acetylacetone and the amount of methyl methacrylate equivalent to the 15 azeotrope distillate are added to the mixture. The mixture is heated to boiling. Alcoholysis is commenced at an overhead temperature of 70°C. Toward the end of the reaction it increased to 100°C.

20 After the end of the alcoholysis the mixture is cooled and the zirconium acetylacetone catalyst is precipitated with dilute phosphoric acid. The suspension is then passed through a pressure filter and the filtrate is separated off.

25 For the purpose of separating off the glycerol carbonate, the filtrate is shaken in a separating funnel containing a dilute NaCl solution. The filtrate is degassed on a rotary evaporator at 70°C and 200-30 10 mbar.

The yield is 87.4%. The purity of the product is 89.7%.

Experiment number: B2

35

Comparative example 1

Isopropyl titanate

236 g (2.0 mol) of glycerol carbonate are heated with 600 g (6.0 mol) of methyl methacrylate and 0.14 g of 4-hydroxy-2,2,6,6-tetramethylpiperidinoxyl (Tempol) in 5 a round-bottomed flask with distillation apparatus. Any water present is distilled off azeotropically with methyl methacrylate. The mixture is then cooled slightly. 8.4 g of isopropyl titanate and the amount of methyl methacrylate equivalent to the azeotrope 10 distillate are added to the mixture. The mixture is heated to boiling. Alcoholysis is commenced at an overhead temperature of 70°C. The reaction, however, is very sluggish, and is therefore terminated after 3 hours, with excess methyl methacrylate (MMA) being 15 removed by distillation. The crude ester is analyzed.

Experiment number: C1

Comparative example 2

20 Dioctyltin oxide

118 g (1.0 mol) of glycerol carbonate are heated with 600 g (6.0 mol) of methyl methacrylate and 0.14 g of 25 4-hydroxy-2,2,6,6-tetramethylpiperidinoxyl (Tempol) in a round-bottomed flask with distillation apparatus. Any water present is distilled off azeotropically with methyl methacrylate. The mixture is then cooled slightly. 14.4 g of dioctyltin oxide and the amount of 30 methyl methacrylate equivalent to the azeotrope distillate are added to the mixture. The mixture is heated to boiling. However, the reaction does not start, no methanol is formed, and the experiment is terminated.

35 Experiment number: C2

Comparative example 3

LiOH/CaO

118 g (1.0 mol) of glycerol carbonate are heated with
5 600 g (6.0 mol) of methyl methacrylate and 0.14 g of
4-hydroxy-2,2,6,6-tetramethylpiperidinoxy1 (Tempol) in
a round-bottomed flask with distillation apparatus. Any
water present is distilled off azeotropically with
methyl methacrylate. The mixture is then cooled
10 slightly. 4.0 g of LiOH, 10.4 g of CaO, and the amount
of methyl methacrylate equivalent to the azeotrope
distillate are added to the mixture. The mixture is
heated to boiling. Alcoholysis is commenced at an
overhead temperature of 70°C. Toward the end of the
15 reaction it increased to 100°C.

Subsequently the batch is cooled and passed through a
pressure filter, and the filtrate is separated off. For
the purpose of separating off the glycerol carbonate,
20 the filtrate is shaken in a separating funnel
containing a dilute NaCl solution. The filtrate is
degassed on a rotary evaporator at 70°C and 200-
10 mbar.

25 The yield is 79.6%. The purity of the product is 52.7%.

Experiment number: C3

Comparative example 4

30 Lithium methoxide

118 g (1.0 mol) of glycerol carbonate are heated with
600 g (6.0 mol) of methyl methacrylate and 0.14 g of
35 4-hydroxy-2,2,6,6-tetramethylpiperidinoxy1 (Tempol) in
a round-bottomed flask with distillation apparatus. Any
water present is distilled off azeotropically with
methyl methacrylate. The mixture is then cooled

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slightly. 14.4 g of lithium methoxide and the amount of methyl methacrylate equivalent to the azeotrope distillate are added to the mixture. The mixture is heated to boiling. Alcoholysis is commenced at an 5 overhead temperature of 70°C. Toward the end of the reaction it increased to 100°C. After the end of the reaction, excess MMA is removed by distillation. The crude ester is filtered and then analyzed.

10 Experiment number: C4

The results of the experiments are summarized in the table below:

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Experiment	Catalyst Amount based on batch in %	Crude ester (containing MMA)				Polytest in MeOH % of th.	Yield % of th.	Monomer pure GC:*		
		Alcohol area%	Product area%	HS1 area%	HS2 area%			Alcohol area%	Product area%	HS1 area%
B1	Zirconium acetylacetone 2.5	8.2	70.1	0.8	0.6	clear	80.6	0.9	91.4	0.9
B2	Zirconium acetylacetone 2.0	8.1	72.7	0.9	0.9	clear	87.4	0.8	89.7	1.0
C1	Isopropyl titanate 1.0	90.7	6.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.3
C2	Dioctyltin oxide# 2.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
C3	LiOH/CaO 2.0	7.5	49.5	12	25	clear	79.6	0.3	52.7	12.3
C4	Lithium methoxide 2.5	2.2	68.9	1.6	20	n.d.	n.d.	n.d.	n.d.	n.d.

Key:

* GC: further peaks
HS 1 glycerol dimethacrylate
HS 2 glycerol trimethacrylate
disregarded

no conversion
n.d. not determined